

## Supporting information

### Temperature-triggered shape-transformations in layer-by-layer microtubes

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## Materials and Methods

**Materials.** Poly(allylamine hydrochloride) (PAH, MW = 58,000 g/mol) was purchased from Sigma Aldrich and poly(acrylic acid) (PAA, MW = 50,000 g/mol) was purchased from Polysciences. Fluorescein isothiocyanate dextran ((FITC-dextran), MW = 10,000 g/mol) was obtained from Sigma Aldrich. All chemicals were used without further purification. PAH and PAA solutions were prepared at a concentration of 10 mM, based on the molar mass of repeat the unit, by dissolving the polymer in 18.2 M $\Omega$ -cm water (Milli-Q, Millipore). The assembly pH of the solution was adjusted using HCl and NaOH. Track-etched polycarbonate (PC) membranes (Nucleopore<sup>TM</sup>) were purchased from Whatman. The membrane's pore size and thickness were 1  $\mu$ m and 10  $\mu$ m, respectively.

**Preparation of FITC-labeled PAH (FITC-PAH).**<sup>1,2</sup> Briefly, 33.6 mg (corresponding to a ratio of 1 FITC molecule for every 100 PAH repeat units) of FITC was dissolved in 400 ml of PAH solution (2 mg/mL in 3:1 methanol-water mixture) and gently stirred overnight. The remaining FITC was removed by extensive dialysis against pure 3:1 methanol-water mixture. Then, the mixture was dialyzed against water for solvent exchange. Dialysis was performed until there was no trace of methanol in the dialysis solution as confirmed by FT-IR spectroscopy (Alpha FT-IR spectrometer, Bruker optics). For LbL assembly, as-made FITC-PAH solution was diluted to 10 mM and pH-adjusted as noted previously.

**LbL microtube preparation.** All samples were assembled using a programmable slide stainer (HMS series, Carl Zeiss Inc.). Polyelectrolyte microtubes were fabricated using a PC membrane as a porous template. PC membranes were first immersed in 10 mM PAH solution for 15 min followed by three separate rinses in pure water for 2 min, 1 min, and 1 min. Then, the PAH-coated membranes were dipped in the 10 mM PAA solution for 15 min followed by another three water rinses as described previously. This process was repeated  $n$  times to yield  $n$  layer pairs, denoted as (PAH/PAA) $_n$  for example. (PAH/PAA) $_n$ PAH denotes the case where PAH is the last layer. Assembly pH-values of 7.5 and 3.5 was used for PAH and PAA, respectively. Following LbL assembly, the LbL-coated membranes were dried overnight at room temperature. Both surfaces of the PC membranes were oxygen plasma-etched for 10 min to remove the film deposited on the membrane surface.<sup>3</sup> PAH/PAA LbL hollow tubes were released by selective dissolution of the membrane in dichloromethane (DCM) followed by sonication for 3 min. Then, PAH/PAA LbL microtubes were washed with fresh DCM three times and ethanol twice followed

by re-dispersion in water at pH 5.5. Then PAH/PAA LbL microtubes were dialyzed against pH 5.5 water for 17 hr to remove residual solvent. PAH/PAA LbL microtubes released from a single membrane were dispersed in 3 ml of water.

**High temperature incubation.** The microtube-in-water suspension (or microtube-in-membrane) was incubated in a temperature-controlled water bath for various times. All samples were sonicated for 3 min prior to incubation. For the incubation at 121 °C, an autoclave (Steris, Amsco Lab250) was used.

**Electron microscopy.** Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-7500F at an acceleration voltage of 5 kV. A few drops of suspension were cast onto a silicon wafer, dried at room temperature, and sputtered with Pt for SEM observation. Transmission electron microscopy (TEM) images were collected using a JEOL 1200 EX operating at a voltage of 100 kV. The suspension was cast and dried on carbon-coated Cu grids for TEM measurements. The length and outer diameter of microtubes were measured from SEM images. We measured at least 30 microtubes and avoided the microtubes that curved significantly because the reading of the dimensions can be affected.

**Modulated differential scanning calorimetry (DSC) measurements.** The thermal properties of bulk PAH/PAA LbL assemblies were characterized using modulated DSC (Q200, TA instruments). PAH/PAA LbL assemblies were assembled on Teflon® substrates, dried in vacuum oven at 30°C overnight, and isolated from the substrate. 18 wt% hydrated samples in pH 5.5 water were prepared according to our previous investigations.<sup>4</sup> Hydrated samples were first prepared by weighing the dried film in Tzero hermetic pans and by adding excess pH 5.5 water. Then, the samples were dried at 40°C to evaporate water until a water content of 18 wt% of the dried film weight was achieved. The total sample weight was around 8-10 mg. Hydrated samples were left at room temperature for 24 hour before measurement. MDSC measurements were performed by employing a heat-cool-heat cycle between 10 °C and 115 °C with amplitude of 1.272 °C for a period of 60 s. All thermal properties were obtained from the second heating scan.

**Confocal laser scanning microscopy (CLSM) measurement.** Optical images of microtubes in water were obtained using CLSM (Leica TCS SP5) with a 63x oil immersion objective. For effective visualization of microtubes, either FITC-PAH or FITC-dextran were used as a fluorescent labels.

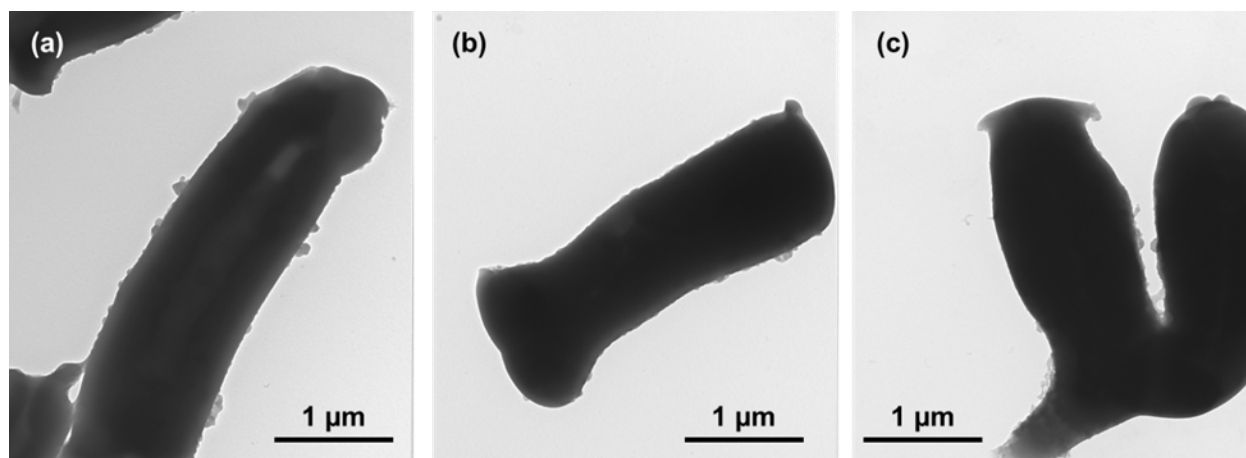


Fig. S1. TEM images of  $(\text{PAH/PAA})_{10}$  microtubes incubated at (a) 25, (b) 85, and (c) 95°C.

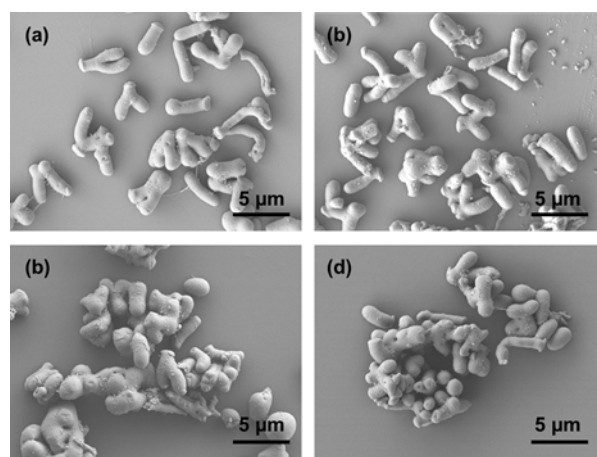


Fig. S2. SEM images of  $(\text{PAH/PAA})_{10}$  microtubes incubated at 70°C for (a) 15 min, (b) 30 min, (c) 2 hr, and (d) 5 hr.

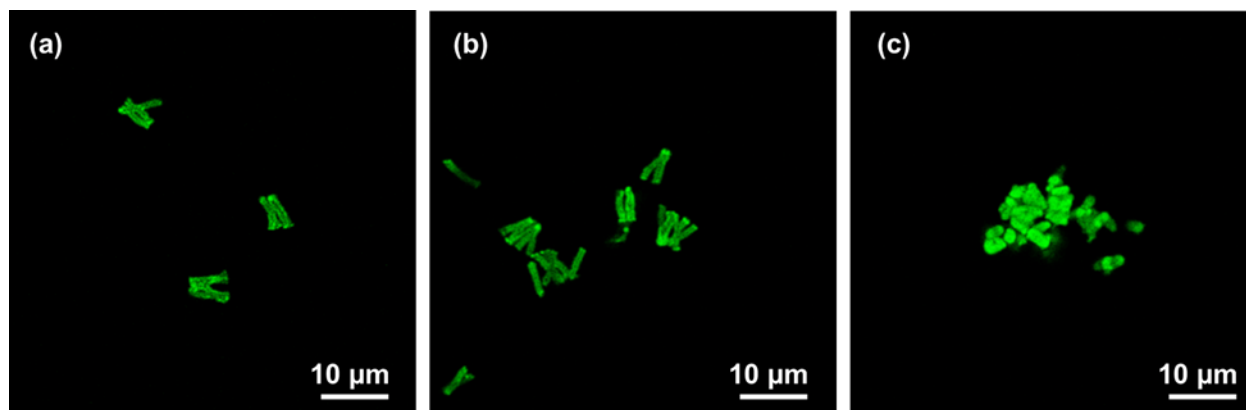


Fig S3. Confocal microscopy images of  $(\text{PAH/PAA})_{10}\text{PAH}$  microtubes in water (a) after dialysis and after incubation at (c) 40 and (d) 95 °C.

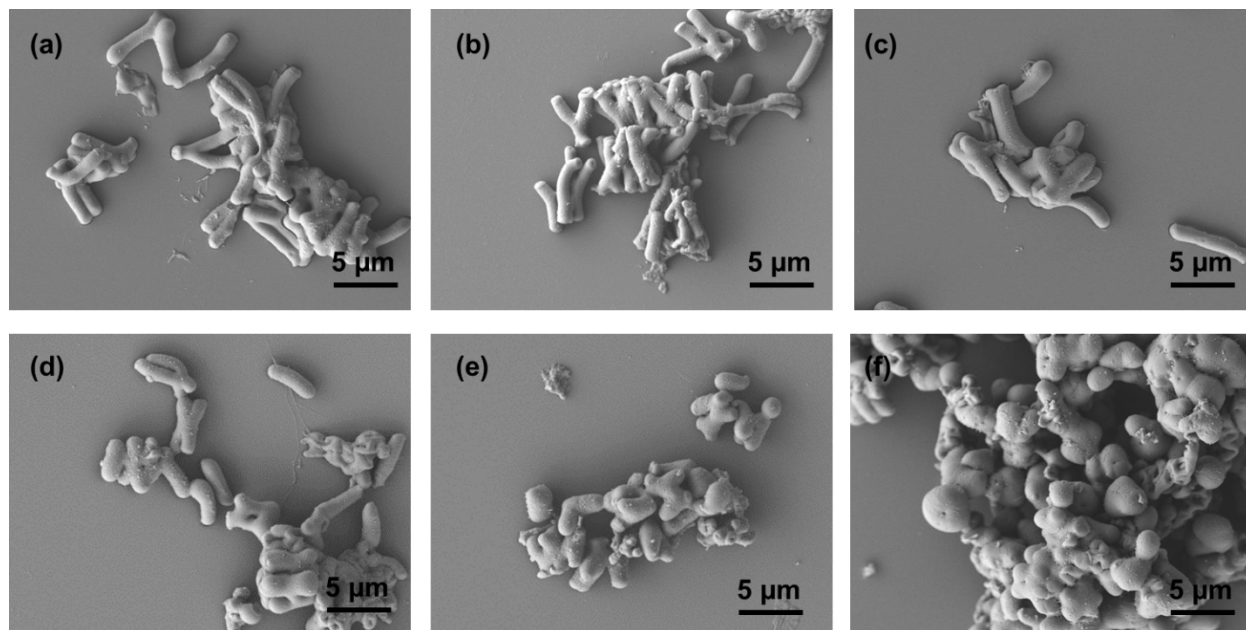


Fig. S4. SEM images of  $(\text{PAH/PAA})_{10}\text{PAH}$  microtubes (a) after dialysis, and after incubation at (b) 40, (c) 55, (d) 70, (e) 95, and (f) 121 °C.

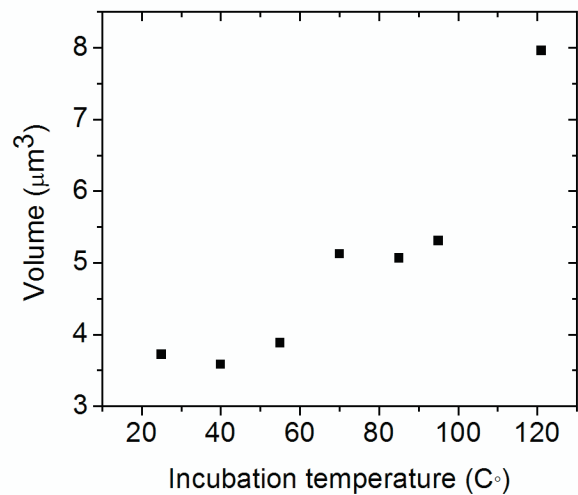


Fig. S5 Microtube volume as a function of incubation temperature calculated from SEM images.

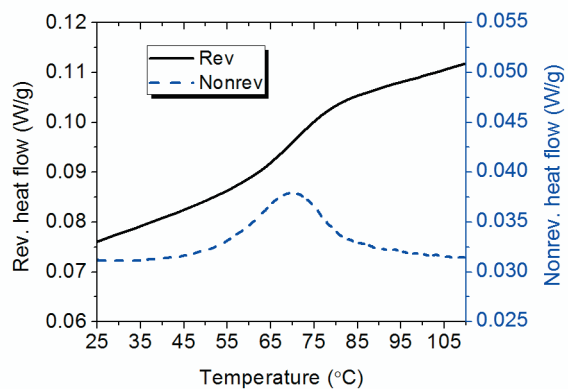


Fig. S6. Modulated DSC thermogram of a hydrated (PAH/PAA)<sub>100</sub> freestanding film.

Table S1. Thermal properties of freestanding PAH/PAA films obtained from the modulated DSC thermogram shown in Fig. S6.

	$T_{\text{init}}$ (°C)	$T_{\text{final}}$ (°C)	$T_{\text{g-m}}$ (°C)	$\Delta T$ (°C)	$\Delta C_p$ (J/(g · °C))
(PAH/PAA) <sub>100</sub>	59 ± 9	80 ± 10	71 ± 7	17 ± 5	0.5 ± 0.1
(PAH/PAA) <sub>100</sub> PAA	62 ± 5	83 ± 5	73 ± 6	20.0 ± 0.5	0.49 ± 0.06

\* $\Delta T$  is the temperature range of glass-melt transition,  $T_{\text{init}}$  and  $T_{\text{final}}$  is initial and final temperature of transition.  $\Delta C_p$  is the heat capacity change during the transition.

## References

1. N. Kato and F. Caruso, *Journal of Physical Chemistry B*, 2005, 109, 19604-19612.
2. A. Schnackel, S. Hiller, U. Reibetanz and E. Donath, *Soft Matter*, 2007, 3, 200-206.
3. K. K. Chia, M. F. Rubner and R. E. Cohen, *Langmuir*, 2009, 25, 14044-14052.
4. A. Vidyasagar, C. Sung, R. Gamble and J. L. Lutkenhaus, *ACS Nano*, 2012, 6, 6174-6184.